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Ambient PAH and Metal Concentration in Intertidal Sediments of Coaster's Harbor and Narragansett Bay

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14. ABSTRACT Previous studies of sediment adjacent to the Old Fire Fighting Training Area (OFFTA) in Coaster's Harbor, Rhode Island, compared values for polynuclear aromatic hydrocarbon (PAH) concentrations for intertidal stations with fully submerged reference stations. NRL and URI have previously reported that the ambient sediment PAH concentrations at that site are low and typical of urbanized estuarine sediments. Bacterial PAH degradation in these sediments results in pool turnover times that suggest the PAH concentrations result from current sources. A Navy fingerprinting study also indicated that the likely source of PAH to Coaster's Harbor sediment is urban runoff. If intertidal and submerged sediments are being impacted by current non-point inputs to surface water, then PAH concentrations may be higher in intertidal sediments. PAHs are relatively hydrophobic and tend to collect at marine interfaces, including the air-sea interface. Wave action in the intertidal zone could deposit hydrophobic contaminants on the surface sediment. An intertidal sediment sampling event was performed in the area adjacent to the OFFTA to evaluate PAH concentrations. In addition, metals analysis was also conducted.					
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AMBIENT PAH AND METAL CONCENTRATION IN INTERTIDAL SEDIMENTS OF COASTER'S HARBOR AND NARRAGANSETT BAY

EXECUTIVE SUMMARY

Previous studies of sediment adjacent to the Old Fire Fighting Training Area in Coaster's Harbor, Rhode Island compared values for PAH concentration for intertidal stations with fully submerged reference stations (Battelle Ocean Sciences 1994, Brown and Root 1997, Montgomery et al. 2003). The Naval Research Laboratory and University of Rhode Island (Montgomery et al. 2003) have previously reported that the ambient sediment PAH concentrations at this site are low and typical of urbanized estuarine sediments. In addition, bacterial PAH degradation in these sediments results in contaminant pool turnover times rapid enough to suggest PAH concentrations result from current non-point sources and not historical input (Montgomery et al. 2003). A recent fingerprinting study conducted by the Navy (Emsbo-Mattingly 2002) also indicated that the likely source of PAH to Coaster's Harbor sediment is surface runoff typical of urbanized areas. If intertidal and submerged sediments are being impacted by current non-point inputs to surface water (e.g. street runoff, ship traffic), then PAH concentrations may be higher in intertidal sediments. PAHs are relatively hydrophobic and tend to collect at marine interfaces including the air-sea interface. Wave action in the intertidal zone could deposit hydrophobic contaminants on the surface sediment. An intertidal sediment sampling event was performed from shore by the Naval Research Laboratory and University of Rhode Island on 12 May 2004 in the area adjacent to the Old Fire Fighting Training Area (OFFTA) and various reference areas to evaluate PAH concentrations and spatial distribution within intertidal sediments. In addition, metals analysis was also conducted to assess concentrations and spatial distribution within the same areas.

PAH Concentration

Total PAH concentrations in nine intertidal sediment samples from Coaster's Harbor and six samples from Narragansett Bay (Figures 1, 2, Table 3) ranged from 0.8 to 24.1 ppm (Table 1). Two of the three highest PAH concentrations (24.1 and 13.5 ppm) were found in the intertidal sediment adjacent to the Middletown boat launch (Latitude: 41°N 34.47000; Longitude: 71°W 17.31040). We previously reported that submerged sediment PAH concentrations near this boat launch reference site were 1.1 ppm (Montgomery et al. 2003). PAH concentrations in the intertidal areas of OFFTA ranged from 1.5 to 21.5 ppm and averaged 7.7 ppm for nine samples whereas the adjacent submerged sediment ranged from 0.11 to 1.3 ppm (Appendix I). PAH concentrations in the six samples from the boat launch and a Tetratex reference area (west side of Narragansett Bay) ranged from 0.8 to 24.1 ppm and averaged 7.1 ppm but the adjacent submerged sediments ranged from 0.03 to 0.22 ppm (Appendix I). For each of these three intertidal sites, the average PAH concentrations from the intertidal sediments are higher than those for the nearby submerged sediment (Montgomery et al. 2003, Appendix I). In addition, the individual PAH compounds that have the highest concentration in the intertidal boat launch sediments (phenanthrene, fluoranthene, and pyrene) are the same compounds that are highest in the most impacted samples from the Coaster's Harbor survey site (Stations 2, 7, 9). These findings support the hypothesis that current surface water inputs are impacting the ambient PAH concentrations in the sediment. Though a major PAH transport study was not performed during the course of this site investigation, the elevated PAH concentrations at the boat launch suggest that local ship traffic may be a significant non-point source. These findings also indicate that submerged reference stations should not be used as reference sites for intertidal sediments because of their differential susceptibility to current day inputs of hydrophobic contaminants to surface waters.

Metal Concentration

Metal concentrations (measured by Battelle Marine Sciences Laboratories, Table 2) in Coaster's Harbor sediment were generally unremarkable relative to that reported for natural soil (http://pubs.usgs.gov/prof/p1634j/html/fm_range.htm) and compared with the reference sites.

Conclusions

This sampling compared intertidal sediment reference sites in Narragansett Bay with intertidal sediments from Coaster's Harbor. Previous samplings of intertidal sediment at Coaster's Harbor were compared with submerged sediment at reference sites. Analyses of data collected in previous samplings of the Coaster's Harbor site by Tetratich (Emsbo-Mattingly 2002), University of Rhode Island (Quinn et al. 1998), Brown and Root Environmental (1997), Battelle Ocean Sciences (1994) and the Naval Research Laboratory (Montgomery et al. 2003) have provided evidence that ambient PAH concentrations are the net result of current day inputs and biodegradation and not the result of historical input. In this study, we found elevated PAH concentrations in the intertidal sediments at both Coaster's Harbor and the boat launch relative to the submerged sediment concentration at both sites. These data support the site conceptual model that non-point source petroleum inputs (e.g. surface runoff, ship traffic) to surface water are the primary influence on ambient PAH concentrations in Coaster's Harbor sediments. Petroleum input via this pathway to these intertidal sediments would be exposed to rapid photodegradation, volatilization, and biodegradation in this relatively high energy environment. The alternate site conceptual model that the PAH concentrations in the submerged and intertidal sediments are the result of historical input is not supported by the data. In the absence of substantial, conflicting information on PAH flux and transport in Coaster's Harbor, it is not scientifically defensible to expect that removal or manipulation of either the submerged or intertidal sediments will result in a net long term reduction in ambient PAH concentrations. In addition, it is recommended that in the future any intertidal sediment samples collected in Coaster's Harbor, adjacent to the OFFTA site, be compared to reference samples that are also collected from intertidal areas with similar environmental influences.

Figure 1. Sample locations for stations 1-9 at OFFTA in Coaster's Harbor for May 2004.

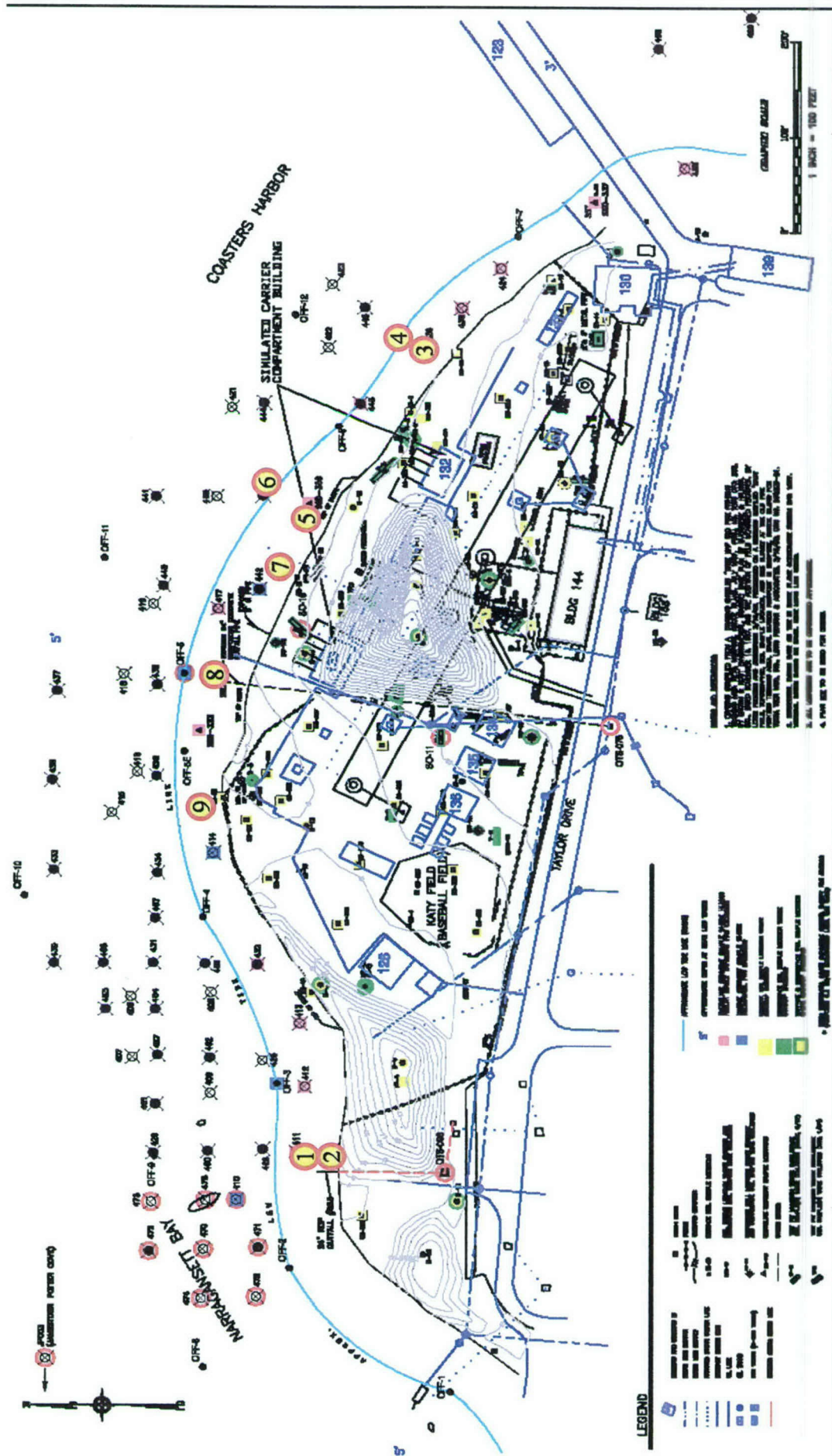


Figure 2. May 2004 sampling stations for Middleton boat launch (Stations 10M (high), 11M (mid), 12M (low water line)) and for the Tetrtech background site on the west side of Narragansett Bay (Stations 13B (high), 14B (mid), 15B (low water line)).

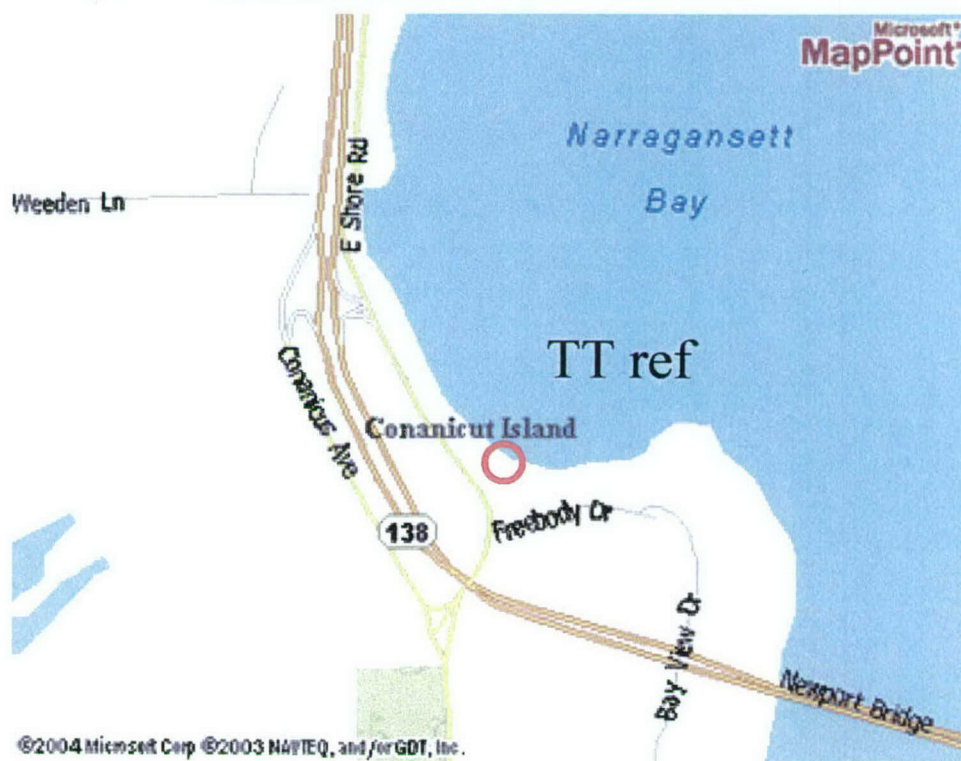


Table 1. Individual and total PAH concentrations (ppm) for intertidal sediment in Coaster's Harbor (Stations 1-9), the Middleton boat launch (Stations 10M-12M), and the west Bay reference site (Stations 13V-15B) for May 2004.

Station	Naphthalene	Acenaphthylene	Biphenyl	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene	Dibenz[a,h]anthracene	Benzo[g,h,i]perylene	Total
1	0.01	0.03	0.00	0.01	0.17	0.04	0.33	0.27	0.12	0.12	0.08	0.09	0.09	0.00	0.06	0.06	1.5
2	0.17	0.95	0.08	0.30	4.61	0.77	5.52	4.51	0.45	0.78	0.72	0.80	0.89	0.11	0.42	0.39	21.5
3	0.02	0.09	0.01	0.04	0.56	0.12	0.75	0.64	0.22	0.19	0.10	0.12	0.12	0.02	0.07	0.07	3.1
4	0.04	0.08	0.01	0.02	0.42	0.10	0.57	0.49	0.13	0.13	0.06	0.07	0.07	0.01	0.04	0.05	2.3
5	0.04	0.23	0.01	0.06	0.98	0.23	1.38	1.05	0.33	0.27	0.13	0.16	0.17	0.01	0.10	0.09	5.2
6	0.12	0.37	0.03	0.11	1.76	0.20	2.43	2.13	0.61	0.48	0.33	0.39	0.43	0.06	0.25	0.25	9.9
7	0.09	0.42	0.02	0.10	2.14	0.44	2.64	1.97	0.59	0.47	0.22	0.26	0.29	0.04	0.16	0.14	10.0
8	0.07	0.30	0.03	0.14	2.84	0.62	2.46	1.91	0.61	0.49	0.24	0.29	0.30	0.04	0.16	0.14	10.6
9	0.06	0.26	0.02	0.14	2.08	0.36	0.12	1.01	0.28	0.23	0.11	0.13	0.14	0.02	0.08	0.06	5.1
10M	0.08	0.00	0.34	0.27	2.64	0.56	2.42	2.39	0.99	0.97	0.56	0.56	0.81	0.11	0.35	0.42	13.5
11M	0.11	0.00	0.71	0.62	5.49	1.20	5.22	4.24	0.47	1.22	1.09	1.18	1.42	0.15	0.27	0.74	24.1
12M	0.01	0.00	0.03	0.03	0.30	0.05	0.34	0.37	0.18	0.21	0.10	0.10	0.16	0.02	0.08	0.09	2.1
13B	0.00	0.07	0.00	0.00	0.07	0.03	0.20	0.20	0.08	0.09	0.05	0.05	0.06	0.01	0.03	0.03	1.0
14B	0.00	0.05	0.01	0.00	0.05	0.03	0.18	0.18	0.07	0.07	0.04	0.04	0.05	0.00	0.03	0.03	0.8
15B	0.00	0.09	0.02	0.01	0.06	0.00	0.17	0.19	0.07	0.07	0.04	0.04	0.05	0.01	0.03	0.03	0.9

Table 2. Metals concentrations (ppm) for intertidal sediment in Coaster's Harbor (Stations 1-9), the Middleton boat launch (Stations 10M-12M), and the west Bay reference site (Stations 13V-15B) for May 2004.

BATTELLE MARINE SCIENCES LABORATORIES													
Jill Brandenberger, Project Manager													
1529 West Sequim Bay Road													
Sequim, Washington 98382													
(360) 681-4564													
SPONSOR	Percent												
CODE	Moisture	Ag		Al		As		Ba		Be		Ca	Cd
	Method:	GFAA		ICP-OES		ICP-MS		ICP-OES		ICP-OES		ICP-OES	ICP-MS
	Digestion:	BA		BA		SE		BA		BA		BA	SE
Achieved MDLs¹		0.0280		7.17		0.0277		0.104		0.0262		1.24	0.0105
Achieved RLs²		0.0890		22.8		0.088		0.331		0.0833		3.94	0.0334
NRL-1	10.2	0.0334	J	40030		5.01		278		1.35		29655	0.203
NRL-2	6.01	0.0327	J	50467		5.21		488		1.99		6872	0.331
NRL-3	7.39	0.0280	U	44128		5.87		325		1.54		57156	0.196
NRL-4	26.2	0.140		41634		4.24		399		1.44		11124	0.283
NRL-5	17.7	0.0404	J	41262		6.60		344		1.29		22158	0.296
NRL-6	25.3	0.0531	J	36540		5.93		335		1.17		26051	0.314
NRL-6	25.3	0.0524	J	40242		4.15		675		1.28		18775	0.285
NRL-7	8.03	0.0677	J	45834		7.91		386		1.51		31217	0.265
NRL-8	10.7	0.0488	J	42254		6.06		337		1.49		24187	0.214
NRL-9	4.18	0.0280	U	46505		15.0		295		1.67		20207	0.204
NRL-10M	3.26	0.0280	U	32911		5.75		275		1.06		5492	0.174
NRL-11M	11.3	0.0280	U	33440		2.84		306		1.05		4997	0.115
NRL-12M	3.55	0.0280	U	33611		4.49		270		1.12		13401	0.131
NRL-13B	18.4	0.0280	U	38723		1.44		335		1.33		4722	0.174
NRL-14B	16.0	0.0280	U	42271		1.63		330		1.53		5765	0.189
NRL-15B	16.9	0.0280	U	36212		1.68		312		1.34		5112	0.242

Table 2. Metals concentrations (ppm; continued).

BATTELLE MARINE SCIENCES LABORATORIES													
Jill Brandenberger, Project Manager													
1529 West Sequim Bay Road													
Sequim, Washington 98382													
(360) 681-4564													
SPONSOR	Percent												
CODE	Moisture	Co	Cr	Cu	Fe	Hg	K	Mg					
	Method:	ICP-MS	ICP-MS	ICP-MS	ICP-OES	CVAA	ICP-OES	ICP-OES					
	Digestion:	SE	SE	SE	BA	SE	BA	BA					
Achieved MDLs¹		0.0103	0.0631	0.153	1.0	0.0043	1.05	1.29					
Achieved RLs²		0.0328	0.201	0.487	3.2	0.014	3.34	4.10					
NRL-1	10.2	7.47	29.1	16.8	20129	0.0315	12643	17189					
NRL-2	6.01	7.28	25.7	19.1	29820	0.0377	18035	7242					
NRL-3	7.39	7.85	22.8	12.5	23434	0.0145	14698	12781					
NRL-4	26.2	6.12	23.5	20.1	21520	0.0190	16820	6150					
NRL-5	17.7	8.11	35.5	19.3	26629	0.0223	15044	5200					
NRL-6	25.3	7.18	31.1	28.9	25071	0.0362	14764	5921					
NRL-6	25.3	5.42	27.6	20.6	51364	0.0327	14289	6029					
NRL-7	8.03	10.2	36.5	22.0	28664	0.0178	17895	9353					
NRL-8	10.7	7.03	34.6	18.4	31443	0.0138	J 16100	6354					
NRL-9	4.18	14.3	33.7	31.9	27233	0.0088	J 16466	11811					
NRL-10M	3.26	8.00	19.1	13.2	25203	0.0118	J 10156	2322					
NRL-11M	11.3	3.65	19.2	8.60	13050	0.0222	12773	2210					
NRL-12M	3.55	4.60	21.2	13.9	15238	0.0107	J 11447	2195					
NRL-13B	18.4	4.88	24.8	10.8	15362	0.0133	J 15055	4174					
NRL-14B	16.0	6.57	24.2	9.90	22802	0.0128	J 16259	4133					
NRL-15B	16.9	5.22	23.1	10.7	17618	0.0127	J 13926	3174					

Table 2. Metals concentrations (ppm; continued).

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Jill Brandenberger, Project Manager																	
1529 West Sequim Bay Road																	
Sequim, Washington 98382																	
(360) 681-4564																	
SPONSOR		Percent		Ni		Pb		Sb		Se		Tl		V		Zn	
CODE		Moisture															
		Method:		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS	
		Digestion:		SE		SE		SE		SE		SE		SE		SE	
Achieved MDLs ¹				0.0538		0.0429		0.00330		0.181		0.0115		0.111		0.459	
Achieved RLs ²				0.171		0.136		0.0105		0.576		0.0366		0.353		1.46	
NRL-1		10.2	14.9		52.8		0.697		0.181	U	0.358		46.2		67.0		
NRL-2		6.01	17.0		52.5		0.738		0.181	U	0.396		46.4		75.1		
NRL-3		7.39	18.8		26.3		0.359		0.181	U	0.183		45.5		94.6		
NRL-4		26.2	12.2		46.8		0.698		0.181	U	0.358		48.5		107		
NRL-5		17.7	17.7		43.3		0.709		0.181	U	0.455		66.5		128		
NRL-6		25.3	17.4		53.1		0.765		0.181	U	0.349		53.7		138		
NRL-6		25.3	13.0		65.3		0.912		0.181	U	0.357		45.6		102		
NRL-7		8.03	21.2		54.2		0.705		0.181	U	0.435		70.2		128		
NRL-8		10.7	16.6		70.2		0.952		0.181	U	0.354		61.3		112		
NRL-9		4.18	22.9		50.9		0.991		0.181	U	0.291		66.3		129		
NRL-10M		3.26	20.6		12.0		0.307		0.181	U	0.286		32.1		95.4		
NRL-11M		11.3	8.36		13.1		0.243		0.181	U	0.289		30.9		54.2		
NRL-12M		3.55	11.4		12.5		0.335		0.181	U	0.331		36.0		78.0		
NRL-13B		18.4	11.2		13.3		0.189		0.181	U	0.366		36.7		59.7		
NRL-14B		16.0	11.2		12.7		0.131		0.181	U	0.372		41.7		61.0		
NRL-15B		16.9	9.61		14.1		0.178		0.181	U	0.345		35.5		63.2		

Table 3. Sample locations for OFFTA stations in Northings and Eastings, or latitude and longitude for reference stations for May 2004.

Station		Coordinates	
NRL	Site	Northing	Easting
1	OFFTA	157003	546800
2		156988	546803
3		156875	547695
4		156890	547706
5		157035	547465
6		157072	547480
7		157098	547395
8		157098	547280
9		157115	547200
		Latitude (41°N)	Longitude (71°W)
10M	Boat Launch	34.4700	17.31040
11M		34.4700	17.31040
12M		34.4700	17.31040
13B	TetraTech Bay Reference	30.6470	21.7300
14B		30.6470	21.7300
15B		30.6470	21.7300

Supporting References

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Appendix I

Data from the second NRL sampling (October 2002) of OFFTA in Coaster's Harbor and reference stations in Narragansett Bay.

Figure A1. Sample locations for stations 1-8 at Coaster's Harbor for October 2002.

Figure A2. Sampling stations for submerged sediment from the Tetrattech background site on the west side of Narragansett Bay (Stations 9), off the McAllister Point landfill (Station 10) and off the Middleton boat launch (Station 11) for October 2002.

Table A1. PAH concentrations in Coaster's Harbor and Narragansett Bay sediment ranged from 0.08 to 1.33 ppm during October 2002 sampling. Ambient PAH concentration was low (< 12 ppm) for three samplings in '02 compared to 6-132 ppm in (Battelle Ocean Sciences 1994), 47 ppm in '97 (Brown and Root Environmental 1997), and to >4 ppm (7 stations), >44 ppm (4 stations) and >132 ppm (1 station) in '98 (Quinn et al. 1998).

Table A2. Mineralization rates for naphthalene, phenanthrene and fluoranthene in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH mineralization rates were consistent with those found in other estuarine sediment sites with low PAH concentration and flux.

Table A3. Turnover times for PAHs in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH turnover was rapid enough to metabolize current PAH flux through sediment in days to months to two years. This is consistent with the attenuation of ambient PAH concentration at the site since 1994.

Table A4. Bacterial production in sediments of Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling was within the range typically found for sediments in urbanized estuaries.

Figure A2. Sampling stations for submerged sediment from the Tetratich background site on the west side of Narragansett Bay (Stations 9), off the McAllister Point landfill (Station 10) and off the Middleton boat launch (Station 11) for October 2002.

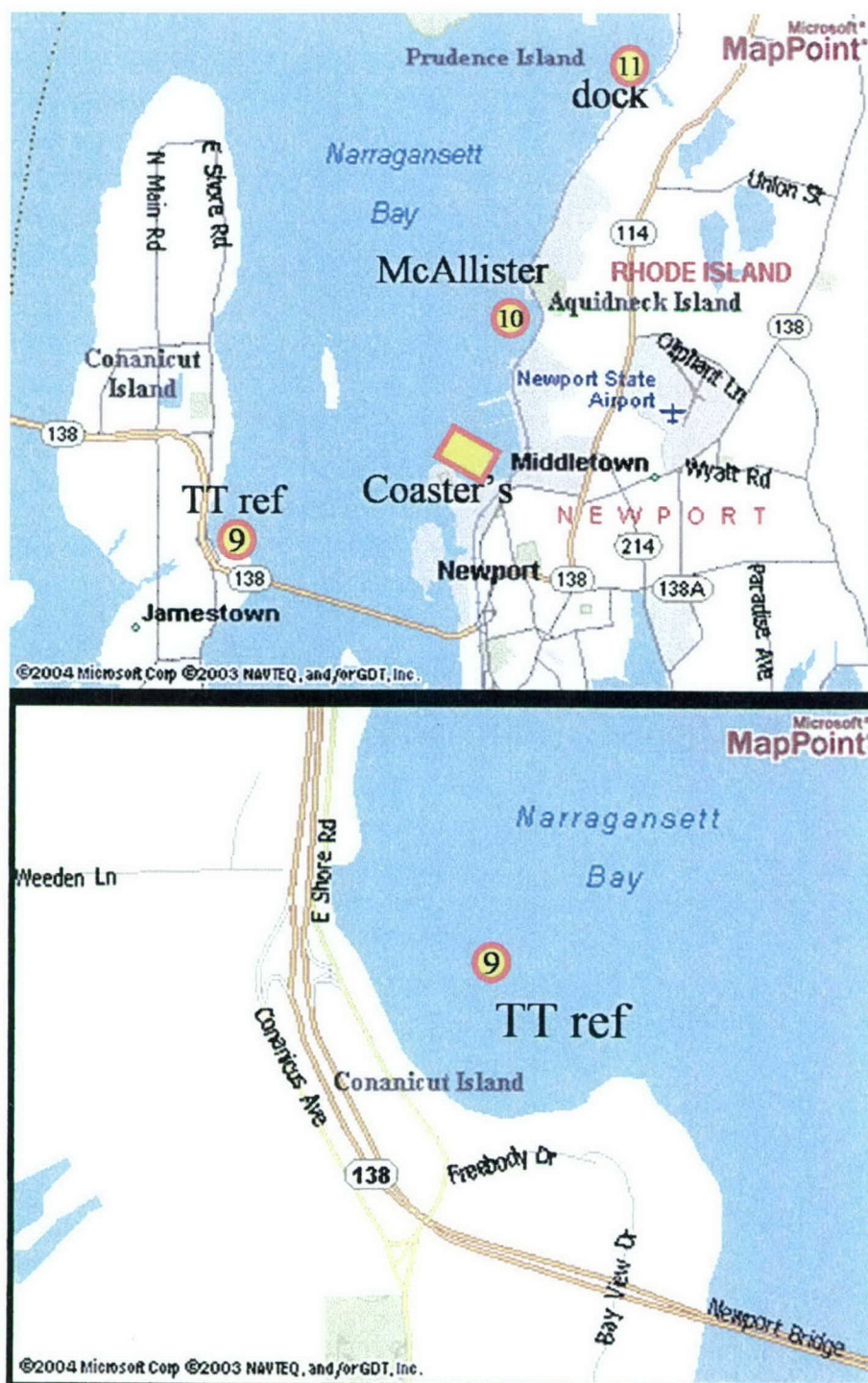


Table A1. PAH concentrations in Coaster's Harbor and Narragansett Bay sediment ranged from 0.08 to 1.33 ppm during October 2002 sampling. Ambient PAH concentration was low (< 12 ppm) for three samplings in '02 compared to 6-132 ppm in (Battelle Ocean Sciences 1994), 47 ppm in '97 (Brown and Root Environmental 1997), and to >4 ppm (7 stations), >44 ppm (4 stations) and >132 ppm (1 station) in '98 (Quinn et al. 1998).

Tetrtech	NRL	Total PAH (ppm)
OFF-3	1	0.96
OFF-2	2	0.24
SSD-337	3	0.98
424	4	1.33
444	5	0.41
417	6	0.15
434	7	0.08
462	8	0.11
Reference	9	0.03
MacAllister	10	0.08
dock	11	0.22

Table A2. Mineralization rates for naphthalene, phenanthrene and fluoranthene in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH mineralization rates were consistent with those found in other estuarine sediment sites with low PAH concentration and flux.

Station	Mineralization Rate ($\mu\text{g g}^{-1} \text{d}^{-1}$)					
	Naphthalene		Phenanthrene		Fluoranthene	
	AVG	SD	AVG	SD	AVG	SD
1	1.09E-05	7.76E-05			2.11E-04	7.26E-04
2			3.50E-03	7.98E-03	1.94E-05	3.36E-05
3	4.67E-04	2.41E-04	2.91E-03	3.24E-03		
4	1.79E-05	6.11E-05				
6	9.67E-04	2.35E-04	3.98E-03	2.55E-03	1.89E-03	2.13E-03
7			5.09E-04	1.11E-02		
8	8.52E-05	1.29E-04				
9	1.38E-04	4.36E-05				
10	3.26E-04	2.20E-04	3.75E-03	1.02E-03		

Table A3. Turnover times for PAHs in Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling. PAH turnover was rapid enough to metabolize current PAH flux through sediment in days to months to two years. This is consistent with the attenuation of ambient PAH concentration at the site since 1994.

Station	PAH Turnover Time (days)	
	Phenanthrene	Fluoranthene
1		939
2	11	3257
3	62	
4		
6	9	18
7	18	
8		
9		
10	4	

Table A4. Bacterial production in sediments of Coaster's Harbor and Narragansett Bay sediment for October 2002 sampling was within the range typically found for sediments in urbanized estuaries.

Station	Sample Type	Bacterial Production ($\mu\text{g C kg}^{-1} \text{ d}^{-1}$)	
		AVG	SD
1	sediment	7.9	2.3
2	sediment	6.7	1.0
3	sediment	20.3	7.5
4	sediment	10.0	3.9
5	sediment	8.7	1.3
6	sediment	11.8	0.9
7	sediment	5.8	1.7
8	sediment	9.7	5.4
9	sediment	9.9	1.5
10	sediment	4.5	0.0
11	sediment	12.4	1.9

Appendix II

Pictures of intertidal locations from May 2004 sampling event.

Figure B1. May 2004 sampling locations at OFFTA for NRL-1, NRL-5, and NRL-8.

Figure B2. May 2004 sampling locations at the Middleton Marina for NRL-10M and NRL-11M.

Figure B3. May 2004 sampling locations near the TetraTech west Narragansett Bay reference site for NRL-14B and NRL-15 M.

Figure B1. May 2004 sampling locations at OFFTA for NRL-1, NRL-5, and NRL-8.

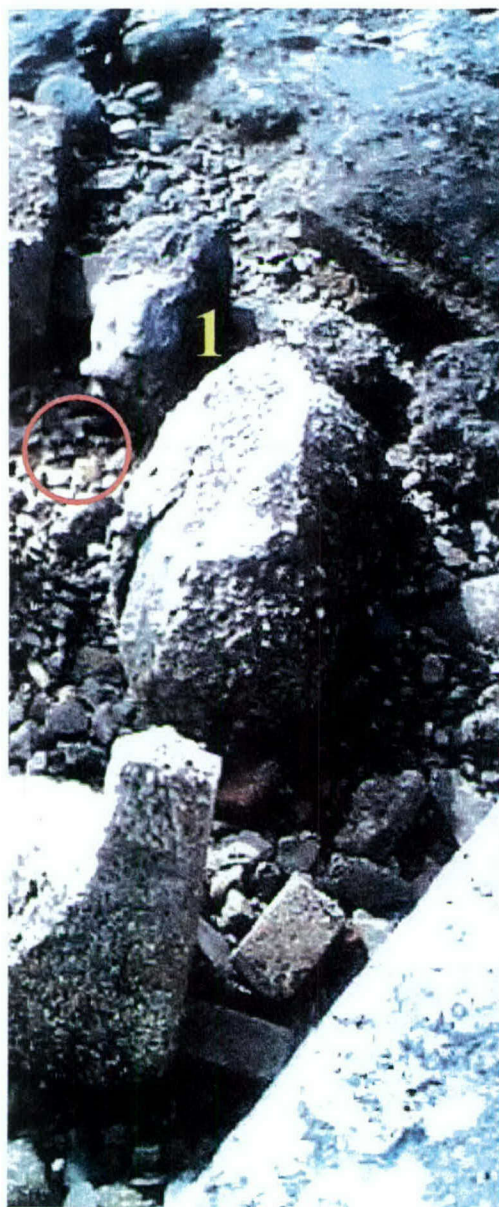


Figure B2. May 2004 sampling locations at the Middleton Marina for NRL-10M and NRL-11M.



Figure B3. May 2004 sampling locations near the TetraTech west Narragansett Bay reference site for NRL-14B and NRL-15M.

